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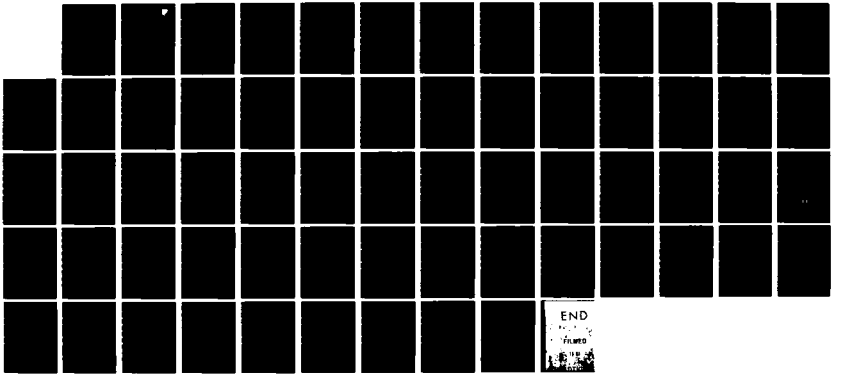

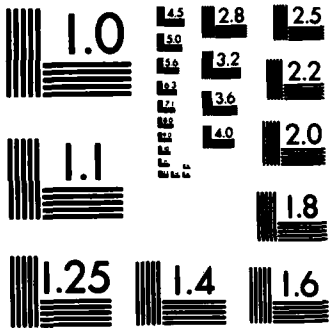

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Interim Report
September 1983

MANUFACTURING TECHNOLOGY FOR HIGH QUALITY SWEPT-CULTURE GROWTH QUARTZ

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Relatively low impurity α-quartz has been grown from the hydroxide mineralizer system with the use of three types of nutrient: converted, special cultured and cultured. The converted nutrient resulted in the lowest total ppm level (2.6) and Al ppm level (0.5) in the as-grown crystals. Special cultured and cultured nutrients resulted in 1.7 ppm and 2.1 ppm of aluminum in crystals grown, respectively, from these nutrients. Infrared Q values ranged from 2.5×10^6 to 1.9×10^6 in these

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crystals.

With respect to ρ in the as-grown crystals, a ten minute etching of seeds in 7.0 molal ammonium bifluoride has resulted in the growth of the lowest etch channel density crystals ($\sim$135cm^{-2}).

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I. INTRODUCTION

Alpha quartz has been employed for many years as crystal oscillators and crystal filters. More recent applications for alpha quartz include employment as high Q resonators in SAW devices and as narrow bandpass optical filters in the near ultraviolet region of the spectrum. As technologies improve, two natural developments occur. One is the better or more efficient utilization of the component materials and the other is the discovery of new potential uses for component parts. Both of these developments require a high degree of reliability in the component materials employed. The component's reliability is important especially with respect to the reproducibility of its desired physical properties.

Two properties of high interest are the frequency stability of quartz resonators in radiation fields and the inherent mechanical strength of high frequency, high precision large surface area resonators. It is important to be able to confidently process alpha quartz into resonators which will exhibit the desired performance requirements. Data gathered over a period of years show that resonators fabricated from low etch channel density quartz have superior mechanical strength than those fabricated from higher channel density quartz.[1] Also, if low etch channel density alpha quartz can be routinely produced,

then chemical etching or polishing techniques can replace certain mechanical lapping procedures which would greatly reduce the number of manipulative transfers. This would allow the greater employment of photolithographic techniques in blank manufacture. It would also allow for the production of a greater variety of blank geometries which would be difficult to produce by mechanical means. Presently, only 33% of natural alpha quartz processed for large surface area blanks result in usable resonators. Therefore, considerable time and effort must be expended to produce a given supply of blanks which meet the desired performance requirements. The same statement can be made for alpha quartz resonators examined for their frequency stability in radiation fields. Presently, no material is routinely available that will consistently withstand exposure to high radiation levels.[2-6]

Therefore, the purpose of this program is the development of a manufacturing method that will produce cultured quartz of such a quality that it will exhibit little or no frequency shifts when exposed to continuous high radiation fields and that the cultured quartz possess a sufficiently low etch channel density so that it may be routinely fabricated into large surface area resonators capable of withstanding a high level of shock.

To meet these objectives, the initial investigations

during the first phase of this program centered upon the variables associated with the hydrothermal growth of alpha quartz. It is useful to break the factors that affect the growth of high purity, low etch channel density quartz into two broad categories: process and component variables. The process variables are those that deal more with the macroscopic considerations during a growth run, such as thermal programming and thermal gradient. These variables have been discussed elsewhere and served as the basis for the investigation of the effect of changes in the component variables on the growth of quartz.[7] The component variables deal more with the microscopic considerations during a growth run, such as the nature and the purity of the mineralizer, the quality and the preparation of the seeds and the quality of the nutrient.

The effect of changes in these component variables and their effect upon the quality of the as-grown quartz were assessed by employing standard characterization procedures for all runs.

II. STANDARD CHARACTERIZATION PROCEDURES

The standard characterization procedures employed can be divided into two broad categories: pregrowth and post-growth procedures.

A. Pregrowth Procedures

The three components that comprise the main variables in any hydrothermal growth run are the nutrient source, the seeds employed, and the mineralizer.

1.0 Nutrient Sources

To date, four different nutrient sources have been examined in our growth runs:

(1) Natural Alpha Quartz (N)

(2) Cultured Alpha Quartz (C)

(3) Special Alpha Quartz (S)

(4) Converted Glassy Quartz (G)

The quality of these nutrient supplies were assessed by atomic absorption spectroscopy. The data on the impurity levels found in these nutrients are shown in Table 1. The converted nutrient was produced by sealing the high purity amorphous quartz in a silver liner with 0.1N sodium hydroxide.[8] This process converts the glassy quartz into alpha quartz

which is then capable of being used as a nutrient source. In this table, the high concentration of sodium listed for the converted nutrient was probably due to the occlusion of some mineralizer in the sample analyzed. As will be shown later, this did not affect the purity of the as-grown crystals produced from this nutrient. The cultured nutrient was prepared from crystals grown from natural quartz nutrient. These crystals were then fragmented and used as nutrient. The special nutrient was prepared from selected crystallized cultured nutrient. The data in this table show that very pure nutrient can be prepared either by a conversion process or by cultured nutrient selection. By these conversion and selection processes the impurity levels in the nutrient supply can be reduced from the 40 ppm range to the 12 ppm range.

2.0 Mineralizers

One of the goals of this program is to develop the manufacturing technology for the growth of high purity - low etch channel density alpha quartz from either the sodium hydroxide or the sodium carbonate mineralizer. Therefore, growth runs have been completed utilizing both mineralizers during this phase of the contract. The mineralizer solutions were analyzed for their starting purity with respect to some of the same elements as the nutrient sources. These data are shown in Table 2. The mineralizers were of equivalent reagent grade quality with neither showing an unexpected

impurity level nor a significant difference in levels between them.

3.0 Selection and Preparation of Seeds

In order to determine the effects of seed preparation procedures on the quality of the crystals grown from these seeds, for the most part, only high Q (2.4×10^6) and low etch channel density seeds ($111 cm^{-2}$) were employed. These seeds were $0^\circ Y$ and each seed possessed good x-ray orientation. In some of the growth runs seeds were employed which were cut from bars that had been electrically swept. All seeds were inspected with a polariscope in order to determine whether or not any strain was present. In the few instances when strain was detected in a seed, the location of the strained area was recorded and the seed was mounted in the growth rack so that it could be properly identified and the as-grown crystal separated upon conclusion of the hydrothermal growth run. During these early growth runs, some seeds were also cut from the plus X region of an as-grown crystal and these seeds were then oriented as a pure Z $0^\circ X$ seed.

Three different etching solutions were employed for seed preparations:

(1) 7.0 molal ammonium bifluoride,

(2) 48% hydrofluoric acid,

(3) 40% ammonium fluoride + 48% hydrofluoric acid.

All three etchants have been used primarily to etch seeds for five and ten minutes, respectively, at room temperature. The ammonium bifluoride etchant, however, has been employed to etch seeds up to 30 minutes in five minute intervals. The third etchant solution listed above was the only etchant used at elevated temperatures and extended etching times. The purpose for this was to attempt to produce chemically polished transparent seeds.

B. Postgrowth Procedures

All the crystals grown in each growth run were inspected individually. The dimensions, and visual perfection of each crystal were recorded, as well as, the weight of the crystals on a tier by tier basis. Depending upon the number of seed preparation variables employed in a given run, crystals were then selected for Q and etch channel density analyses. Sample preparation for both Q and ρ determinations was identical. Y-cut and AT-cut slices were removed from each selected single crystal. The slices were cut to a thickness of 6.35mm and then these slices were consecutively lapped with 25 micron and 3 micron aluminum oxide abrasives to a final thickness of 6.00mm.

1.0 Q Determinations

A Beckman ACTA MIV spectrophotometer was employed for the Q determinations with a wavelength accuracy and resolution

better than 2.5nm and 1.2nm respectively. The equation used for this determination was:

$$\frac{10^6}{Q} = -0.45\alpha^2 + 7.47\alpha + 0.114 \text{ (2631.6 \& 2857.1nm)}$$

In order to properly characterize the Q of the as-grown quartz, the sample should be linearly translated through the beam so that a complete profile along the Z axis is obtained.[9]

2.0 Etch Channel Density Determinations

The etchant solution chosen was ammonium bifluoride. This solution was chosen because an experimental base was already developed independently. The length of etch was fixed at two hours at a temperature of 75°C. Variables that still had to be determined were the concentration of the ammonium bifluoride, the number of 'AT' slices to be etched per solution volume, and the expected variation of the etch channel density within a crystal, as well as, within a growth run.

Multiple 'AT' slices were cut and lapped from three stones which had previously exhibited high etch channel densities. Two slices from each stone were etched with different concentrations of ammonium bifluoride under the same time and temperature conditions above (Figure 1). These data indicated that a relatively constant etch channel density was obtained with a solution concentration of 24 molal. It was also noted that a large change in channel density occurred in all three

samples between the etchings performed at 9 and 12 molal ammonium bifluoride. Since the solutions were always agitated during the etching process, it was not thought that the change in density was related to a change between diffusion controlled and reaction controlled kinetics.

In order to determine the change in etch channel density within an as-grown crystal and within the growth zone, crystals were selected from an earlier growth run which had exhibited a high etch channel density from prior analysis. Multiple slices from a test crystal in the top tier were cut and lapped along with a slice from a crystal from the bottom tier of the growth zone. All ten slices were then etched at the same time and the channel densities determined. Table 3 contains these data. The slices from the top test crystal were numbered consecutively from one end of the crystal to the other. Seven of the nine density determinations were within one standard deviation of the average value for the top test crystal. The etch channel density of the slice from the bottom test crystal compared quite favorably with both the average ρ of the top test crystal and the value at the same position (which could be either position #1 or #9 of the top test). Figure 2 is a graphical representation of these data. Interestingly, if one looks at the values from the opposite ends of the top test, there is even a better correlation between values. That is, it appears as if the channel densities can be paired, such as #1 and #9, #2 and #8, etc. The only value that does not fit this is that measured

on slice #6. The indication is that there may be a twofold axis with respect to channel density. Our main interest here, however, was to develop confidence that a particular slice from an as-grown crystal would sufficiently characterize the quality of most crystals grown in a particular growth run with respect to ρ. The data, to date, do indicate that a slice from a crystal would serve as a reasonable indication of the average etch channel density in a run. Also, this allowed us a greater degree of freedom in the location and number of seeds, which were prepared by different means, that could be used in a particular growth run.

The last variable in the etching process that had to be determined was the number of samples that could be etched per unit of solution and obtain repeatable etch channel densities. Again multiple slices were cut from three crystals and these slices were lapped and then etched in 0.5 liters of 24.0 molal ammonium bifluoride. The number of slices was varied from 4 to 15 per load. To reach the prescribed sample numbers per load, dummy slices were added to the solutions. These dummy slices were equivalent Y-cut slices that had been through an equivalent stage of the test procedure. Table 4 contains these data. These data indicate that up to 8 slices can be etched at one time in the standardized solution without affecting any significant change in ρ between the slices from the same crystal. Less consistent etch channel densities were found at

the 15 sample loading when compared to the determinations on the respective crystals at the other sample loadings. A summary of the complete etching procedure that is being employed during this investigation is shown in Table 5.

3.0 Electrical Sweeping

Crystals which served as seed material for some runs were electrically swept. In addition, after postgrowth analyses of a run were completed, crystals were selected for fabrication into bars for electrical sweeping runs. Figure 3 is a schematic of the sweeping arrangement employed. This arrangement was modeled after that described by Lipson et al.[10] The electric field employed during these runs ranged between 1.0 to 2.5 KV/cm. The sweeping temperature was maintained at 500°C and platinum electrodes were used. All sweeping runs were conducted in air. The data gathered during these runs coincided with the published results of Brown et al.[11]

III. RESULTS AND DISCUSSIONS

To date thirteen hydrothermal growth runs have been completed. Of these, bars from eleven of these runs have been submitted for fabrication into either AT or SC blanks and some of these bars were electrically swept. Two of these thirteen runs have just completed their growth cycles and only growth run data have been completed. One of these runs utilized sodium carbonate as the mineralizer (CC-12) and the other sodium hydroxide (CC-13). In order to discuss the results of these runs in a reasonable manner, it is necessary to divide the runs into three groups: those conducted in a large autoclave with Na_2CO_3; those conducted in a large autoclave with NaOH and those conducted in a small autoclave with NaOH. Tables 6-8 list the growth run data collected on these runs by vessel category. These tables contain the important pressure-temperature, thermal gradient and dimensional data recorded for each growth run. Also, the nutrient type is listed for each run in these tables. What is not listed is the Q and ρ data determined on selected sample crystals analyzed in each run. These data will be presented when the effect of seed preparation procedures on the growth of the crystals are discussed.

Columns three and four, in these tables, list the average crystallization temperature and the average thermal gradient, respectively, employed for each growth run. The last column

in each table contains the type of nutrient employed for the particular run. The remaining columns deal with the average Z dimension and its standard deviation, the Z rate and the Z range for each run as determined by the measurement of all crystals grown in the run. The Z range has not been listed for the runs conducted in the experimental vessel because the number of crystals grown per run was small.

Comparison of the data in Tables 6 and 7 shows that the average Z growth rate in the hydroxide mineralizer runs was approximately 50% higher than the average Z growth rate in the carbonate mineralizer runs. This calculation was done by neglecting run CC5 which contained a different seed loading compared to the rest of the runs listed in Table 7. However, the average variation in Z dimension, as measured by the standard deviation was, 20% less than the average standard deviation in the carbonate runs. This indicates a better uniformity of growth was obtained in the hydroxide mineralizer growth runs. The Z range was found by subtracting the longest Z dimension crystal from the smallest in the same run. In this case, an 8% greater variation was found in the hydroxide mineralizer runs. However, since there were 20% more crystals grown in these hydroxide runs when compared to the carbonate runs, it is evident that the Z dimension range is not as significant as the average Z value and its standard deviation.

The runs conducted in the small autoclave must be considered as a separate group because this vessel was employed to study more closely the effect of nutrient quality and special seed preparation and selection techniques in addition to those listed in Section 3.0 of the Standard Characterization Procedures. Three of the four runs listed in Table 8 were conducted under similar conditions and can be considered one group. One run in this table (CC7) is unique. The average Z growth rate of the group (.84mm/day) was 8% greater than the NaOH group listed in Table 7 and 65% greater than the Na_2CO_3 group listed in Table 6. Yet, as will be shown below, the Q values of this group were consistently over $2x10^6$ which was not the case in the other groups, especially the carbonate runs.

The results of the growth runs conducted in the experimental vessel with respect to Q, ρ and impurity levels are shown in Tables 9 and 10. Table 9 contains data pertaining to the variation of Q and ρ with respect to seed quality and preparation. The seeds employed in runs CC2 and CC4 were etched for five minutes in 7.0 molal ammonium bifluoride. In CC4, the seeds were cut from an electrically swept pure Z 0°Y quartz bar before etching. Both of these runs employed cultured nutrient. CC10 employed chemically polished 0°X and specially selected quartz nutrient. Run CC7 used nutrient converted from optical grade quartz and plus Y seeds oriented as pure Z seeds but were of unknown quality. The data in

Table 9 show that neither electrically swept seeds nor seeds cut from the plus X region will necessarily result in low etch channel density as-grown crystals. Even seeds with extremely low etch channel density, as were the electrically swept seeds, does not guarantee a low ρ. The data do show, however, that one can grow high Q alpha quartz regardless of the Q or ρ of the seeds employed. Finally, there is no correlation between the crystal Q and ρ as determined in these runs. To summarize the important features of Table 9:

(1) Low ρ seeds do not guarantee low ρ crystals,

(2) Variable quality seeds can grow high Q crystals,

(3) No correlation is evident between crystal Q and and crystal ρ,

(4) High growth rates can yield high Q alpha quartz with a moderately low etch channel density.

Table 10 lists the impurity levels found in the crystals grown in the experimental vessel runs. Sections from the same crystals were used for this analysis that were employed for the Q and ρ data listed in Table 9. One can calculate a relative distribution coefficient for these impurities by using the concentrations of these impurities in the as-grown crystal to the concentrations found in the nutrient supply used in those runs. That is, it was necessary to neglect the actual concentration of these impurities in the solution, as well as, other sources of impurities such as the vessel walls, nutrient baskets, seed racks and the mineralizer itself.

The vessel components would necessarily be an additional source of iron and the mineralizer contains substantial amounts of sodium and lithium. Aluminum, and possibly potassium, are the only cationic species whose major concentration ought to be from the nutrient supply. Strictly speaking, the distribution coefficient is the ratio of the concentration of the impurity in the crystal to the concentration of that impurity found in the solution (mineralizer). However, since a limited amount of analyses have been performed on the mineralizers after growth, it was necessary to make the above assumptions. Table 11 contains these data. These data were calculated from the data listed in Tables 1 and 10. Some interesting results can be seen from these data. The relative distribution coefficients for Na and Li are both less than unity. Considering the relatively high concentration of both of these cations in solution, this indicates a very good rate of rejection for both species in the as-grown crystal. The crystals grown from the converted nutrient yielded the lowest relative distribution coefficients for both cations. It should be noted that all runs were carried out in regular unlined autoclaves.

The k_K for all runs listed here was greater than or equal to unity. However, the actual ppm levels in the as-grown crystals were extremely low ($\leq$0.8 ppm). In these runs, this impurity does not appear to be a major factor. The

ionic radius of potassium is approximately 30% greater than that of sodium with the same coordination number. Therefore, one would not expect to find a high concentration, relative to sodium, in the quartz lattice. The last two cation impurities are usually considered to be substitutional rather than interstitial in the quartz lattice. The relative distribution coefficient of aluminum was found to be considerably less than one in all cases with the best results obtained utilizing the converted nutrient. In this case, a general trend in the coefficient had occurred with the successive use of higher quality nutrient. That is, as the ppm level of the aluminum decreased in the nutrient source, a greater rate of rejection in the crystal also resulted. The last impurity element analyzed was iron. Here, varied results were obtained. In the two instances where some form of cultured nutrient was used, the k_{Fe} was greater than unity and in the converted nutrient case, k_{Fe} was 0.2. Whether this is related to the nutrient source or related to the thermal programming conditions employed has not yet been resolved. Runs are in progress with the special cultured nutrient under similar programming procedures employed in CC7. What the data do show is that a futher contamination of the crystal had occurred and this contamination is the result of the vessel itself or the steel parts used to hold the nutrient and the seeds. To summarize the more important results of Tables 9, 10, and 11:

(1) High purity quartz crystals appear to be able to be produced utilizing either the converted or special cultured nutrient,

(2) The Q of the crystal is not related to the total impurity content of the crystal,

(3) A substantial rate of rejection exists for Li, Na and Al,

(4) Etch channel density is not related to the impurity levels,

(5) Seed preparation techniques affect channel formation but not Q.

The next group of runs that can be considered as a group are those listed in Table 7. In these runs, a wider variety of seed preparation techniques were employed. Run GC5 was done in order to establish the effect of seed preparation techniques on etch channel density. In this run seeds were either etched in ammonium bifluoride or HF from 5 to 60 minutes. Also, seeds were cut from electrically swept bars and these were etched for 5 minutes in 7.0 molal ammonium bifluoride. Table 12 contains selected results obtained on the crystals analyzed in this run. In this table ABF is the ammonium bifluoride etchant and all etch times are in minutes. These data indicated that seed preparation plays an important role in etch channel formation and that the quality of the seed, with respect to ρ, may not be a governing factor. That is, seeds with a known low etch channel density do not necessarily result in a crystal with low etch channel density. The converse of this also appears to be true. This run also

indicated that the type of etchant employed and the length of etching time played a role in channel formation. The seed preparation conditions employed in all runs after GC5 were based upon the broad spectrum of results obtained in GC5. Typical impurity levels, in ppm by weight, in GC5 were Li:0.8; Na:3.6; K:0.7; Al:4.6 and Fe:1.5.

In order to control the seed quality variable in the subsequent runs only high Q (2.342×10^6) and low etch channel density seeds (111cm^{-2}) were employed. Each seed was viewed under crossed polarizers to determine if any strained areas were present and all seeds were 0^{o}X. Each seed was also identified with respect to its location in each seed tier in each run. The three etchant solutions listed in Section 3.0, Selection and Preparation of Seeds, were employed in runs GC6, GC9, GC11 and GC13. Tables 13, 14 and 15 contain the data collected on the crystals analyzed in these runs. The data in Table 13 compare some critical parameters with respect to the specific etching conditions employed for the seeds used to grow the crystals that were analyzed. The average values and their standard deviations are shown for the Z rate, $\overline{Q}$ and $\overline{\rho}$ determinations. The standard deviations listed in this table were calculated using a minimum of six test samples per parameter category. From this table it appears that the ten minute seed etchings result in, on the average, crystals that have a higher average $\overline{Q}$ and a lower average $\overline{\rho}$ with a slightly lower average growth rate than the crystals grown from seeds etched for five

minutes. In both groupings, it was discovered that the ammonium bifluoride seed etchant resulted in the growth of crystals which exhibited high $\bar{Q}$ and the lowest $\bar{\rho}$. If we group the data by seed etchant without regard to etch time (Table 14) we find that the crystals grown from seeds etched in ABF have the highest average Z growth rate, high $\bar{Q}$ and the lowest $\bar{\rho}$ of any of the etchants studied in this range.

From these results runs CC9 and CC11 were used to grow crystals from seeds which had extended etching times in ammonium bifluoride, as well as, seeds chemically polished by the ammonium fluoride - hydrofluoric acid mixture at elevated temperatures. Table 15 compares the results obtained through the analysis of crystals grown from these specially prepared seeds. These data indicate that extended etching tends to degrade the quality of the as-grown crystal with respect to its etch channel density. Also, the seeds that were chemically polished resulted in the growth of crystals that exhibited high channel density. The data in this latter case are based upon a small number of samples analyzed. It also should be noted that all of the data presented so far in this report, with one exception, was gathered from crystals grown from seeds which had no evidence of strain as judged by our polariscope testing. The one exception was the data collected from the crystals analyzed in run CC7 (Table 9). The effect of strain on etch channel density is shown in Table 16. These data were gathered from crystals grown from seeds that were

etched in 7.0 molal ammonium bifluoride at room temperature. It is evident from these data that any strain in the seed results in a higher channel density. Also, there is an indication that a seed prepared from any other growth region in the crystal, other than the pure Z region, results in excessively high channel density.

To date, only one run in this group (CC6) has been analyzed for the uptake of impurities. These data are shown in Table 17. Substantially low total ppm levels were realized in this run with reasonably low etch channel densities in the crystals grown from seeds etched for ten minutes in ammonium bifluoride. In fact, the total impurity level is only a factor of two greater than that found in run CC7 which utilized converted nutrient.

To summarize the more important results of Tables 12 through 17:

(1) Low or high ρ seeds do not result necessarily in low or high ρ,

(2) There is no advantage in employing seeds cut from electrically swept quartz, as far as ρ is concerned,

(3) Etching seeds for ten minutes at room temperature is beneficial with respect to Q and ρ for the as-grown crystal,

(4) Ammonium bifluoride appears to be the best free etchant, to date, for seed preparation,

(5) Extended seed etching times degrades the as-grown quartz with respect to ρ,

(6) Strained seeds result in greatly increased etch channel densities in the as-grown stone,

(7) Relatively low ppm crystals can be grown in a large size production vessel with cultured quartz nutrient.

The last group of runs to be analyzed for the first year's investigation in this initial phase of this program are those runs employing Na_2CO_3 as the mineralizer. To date, three runs have been completed but, complete data are available only on the first two (GC1 and GC8). GC1 was essentially a replica of run GC5 which utilized NaOH as the mineralizer. That is, this run was an attempt to determine the effect of seed preparation techniques on etch channel density by employing a wide quality of seeds. The data gathered from the analyses of crystals grown in this run are shown in Table 18. This was the first attempt to grow large pure Z quartz crystals for this program. The data listed in Table 18 again indicate that the ammonium bifluoride etchant for the seeds yielded crystals which, on the average, possessed a low etch channel density. We have also discovered that the carbonate mineralizer is much more sensitive to temperature changes than the hydroxide mineralizer for large pure Z crystal growth. This is evidenced by the lower Q values listed for the crystals analyzed. Run GC8 employed the same seed quality used in runs

CC6 through CC11. In this run both strained and unstrained seeds were employed in order to determine the effect of strain in the carbonate mineralizer. A comparison of the data collected on the crystals analyzed in this run are listed in Table 19. A significant improvement in Q was realized by changing the thermal programming procedure as compared to CC1. Also, additional data gathered in this run show that strained seeds do result in a significantly higher channel density in the grown crystal than do unstrained or clear seeds. It also appears that growth on strained seeds result in a lower Q crystal. One piece of datum gathered in this run that did not fit the results gathered in the hydroxide system was the low ρ measured on the crystal grown from the seed etched in the 48% HF + 40% ammonium fluoride solution. Previous data indicated that a higher channel density should have been obtained. More data will be gathered from run CC12 with respect to this etchant solution. A comparison of impurity levels in crystals grown from strained and clear seeds was also done and these data are listed in Table 20. From these data it appears that a crystal grown from a strained seed has a tendency to incorporate more impurities than a crystal grown from an unstrained seed. If one compares the impurity levels in the crystal grown from the clear seed with the impurity levels found in a crystal grown from a clear seed in a hydroxide mineralizer run (Table 17), there appears to be a difference in the total impurity levels found in the crystals. A lower total ppm level

was found in the hydroxide grown crystals. Whether or not this is always the case cannot be stated yet. More data must be gathered from crystals grown from similarly prepared seeds, as well as, crystals which exhibit the same Q and ρ levels.

The final test, as to whether or not crystals of a certain purity level and Q value are acceptable, is the performance of blanks fabricated from these crystals. Lumbered bars have been cut from crystals grown in the runs listed in this report and have been submitted for blank fabrication. The blank specifications and the runs from which the lumbered bars were fabricated are listed in Table 21. The table is divided into four rows. All items listed in the first row (through CC4) have resulted in delivered blanks and the doubly-rotated blanks were fabricated from electrically swept material. Lumbered bars have been submitted for all the remaining rows but no blanks have yet to be received. The delivery of these blanks should be near the end of May, 1983. All other runs (CC12 and thereafter) will result in the submission of only electrically swept lumbered bars for blank fabrication. The submissions prior to CC12 served for the formation of a blank data base for this program with which future submissions could be compared.

IV. SUMMARY AND CONCLUSIONS

The purpose of this program is twofold, that is, the development of a manufacturing method for the growth of low aluminum content α-quartz capable of operation in a high radiation environment and the development of a method for the production of low etch channel density quartz capable of being fabricated by photolithographic means. To date, progress has been made toward both goals.

Relatively low impurity α-quartz has been grown from the hydroxide mineralizer system with the use of three types of nutrient: converted, special cultured and cultured. The converted nutrient resulted in the growth of α-quartz with a total impurity content of 2.6 ppm and 0.5 ppm Al. The special and the cultured nutrient supplies resulted in the growth of crystals with total impurity levels of 8.7 ppm and 5.4 ppm respectively and aluminum levels of 1.7 ppm and 2.1 ppm. The O values, as determined by the infrared method described earlier, ranged from 2.5×10^6 to 1.9×10^6 in these samples.

To reduce further these impurity levels, runs are now being conducted with modified thermal programming procedures and more careful cultured nutrient preparation and selection. That is, the distribution coefficient of these impurities can be lowered further by programming changes and these changes

should also increase the Q value measured for the crystals. It may be necessary to employ an inert liner to reduce the impurity levels, say, to the 0.2 ppm range or less per impurity ion. This judgement will be made based upon the results obtained in the growth runs now in progress.

With respect to the reduction of etch channel densities in the as-grown crystal, more investigations into seed preparation techniques are in progress. Presently, a ten minute etching of seeds by ammonium bifluoride seems to result in a channel density of approximately 135cm^{-2}. The goal is to reduce this value to below 50cm^{-2} in the as-grown crystal. In order to reach this goal seeds are being cut from seed crystals with various finishes and these seeds are being subjected to free and insitu etching procedures utilizing primarily the 48% HF + 40% NH_4F etching solution at elevated temperatures. These results will then be compared to the results already obtained and a decision then will be made on the final seed preparation direction to pursue.

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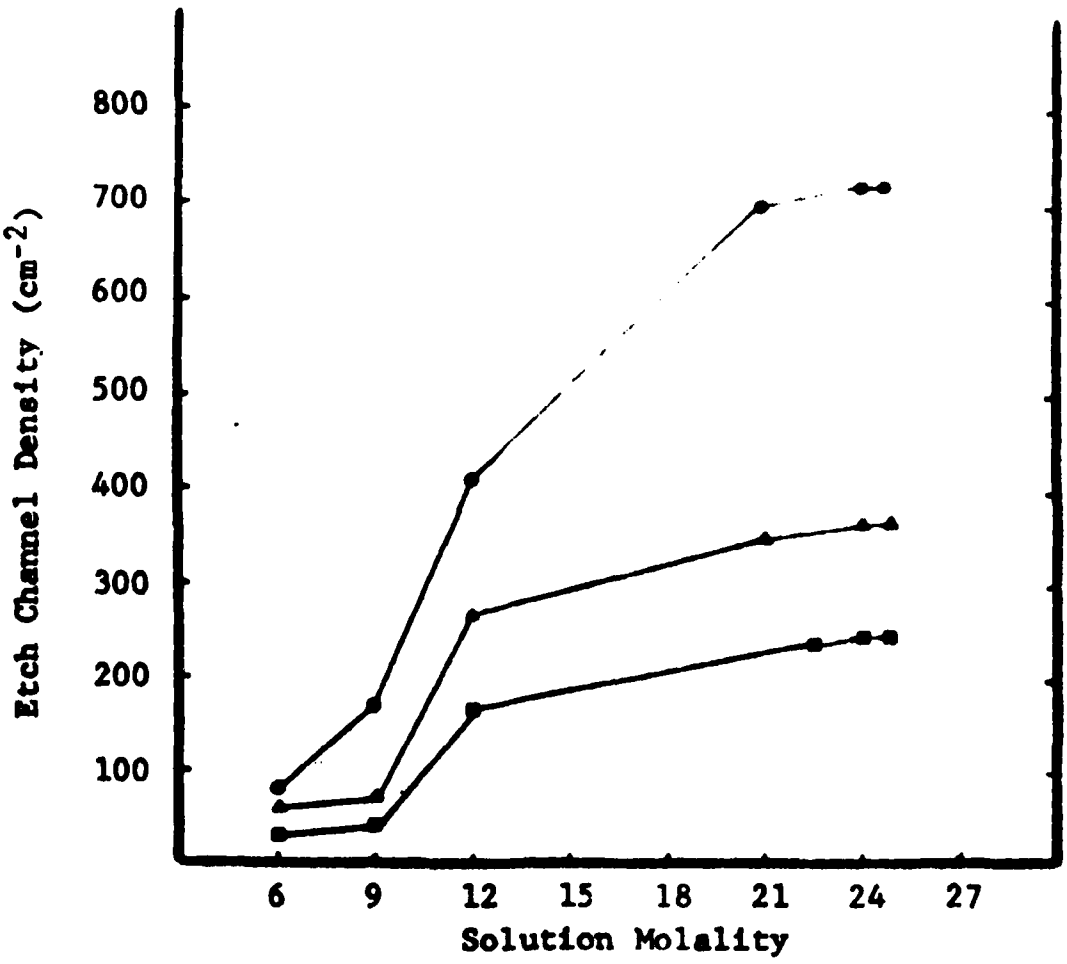
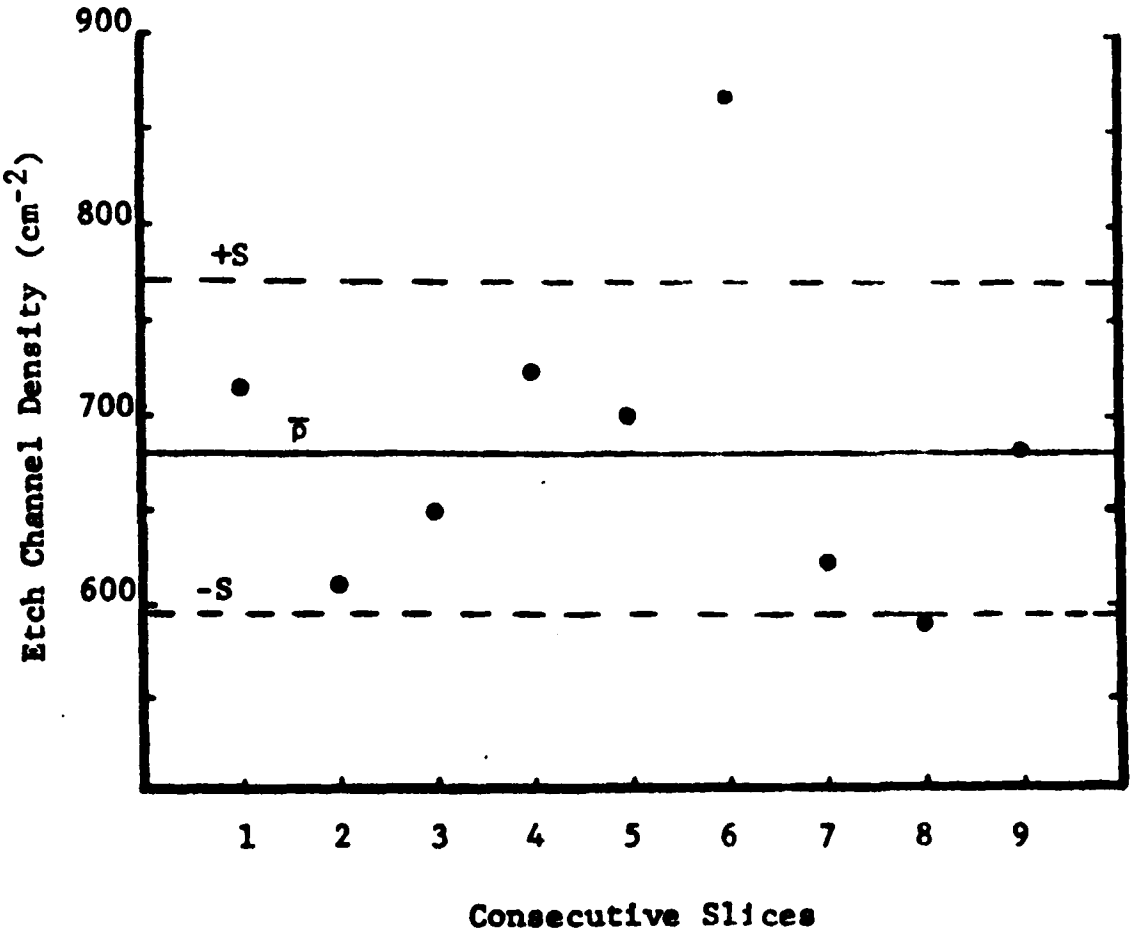
VI. FIGURES

FIGURE 1



CHANGE IN ρ AS A FUNCTION
OF SOLUTION MOLALITY FOR
THREE DIFFERENT CRYSTALS

FIGURE 2



TYPICAL CHANNEL DENSITY VARIATION
WITHIN ONE AS-GROWN CRYSTAL

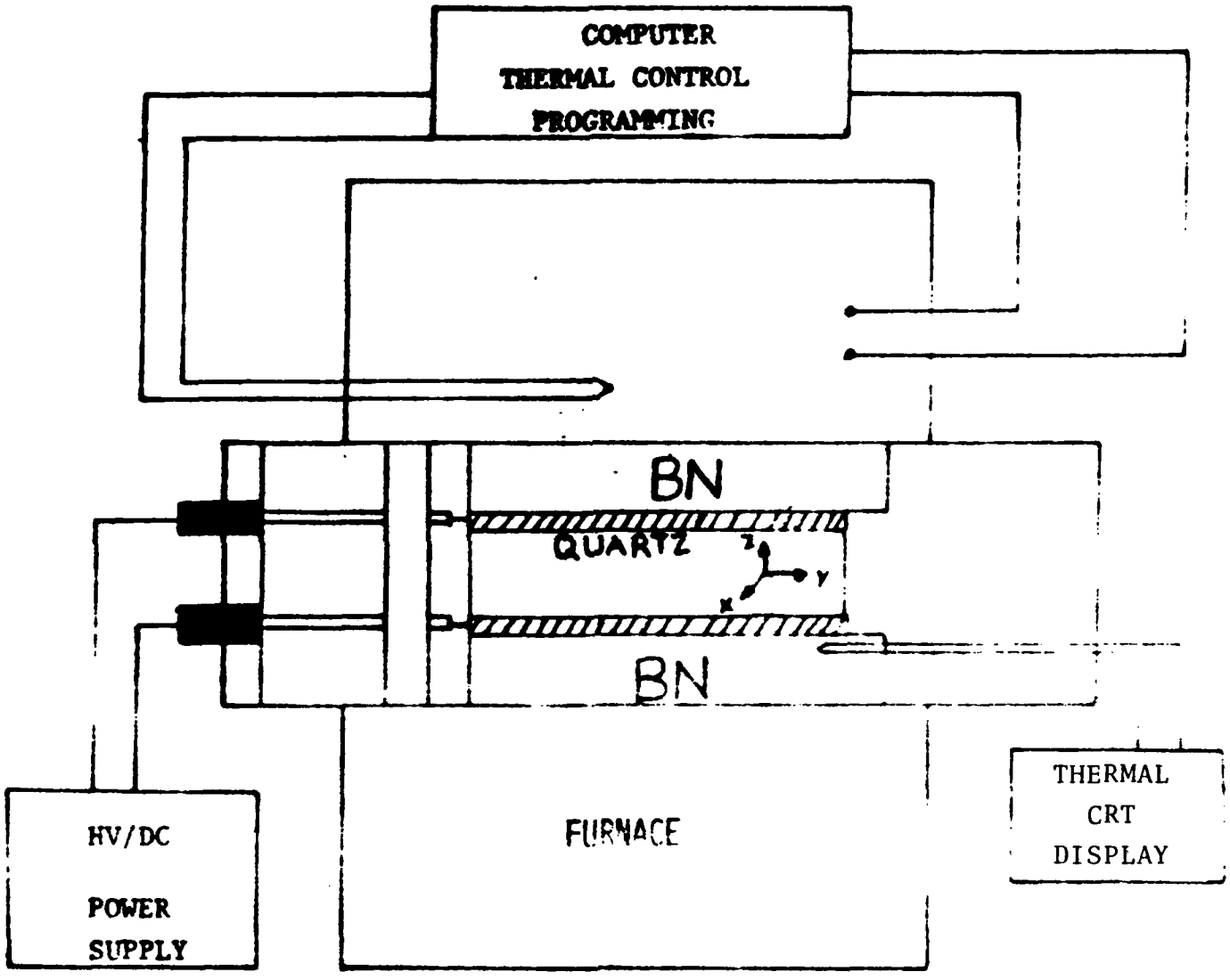


FIGURE 3

SCHEMATIC OF SWEEPING APPARATUS

VII. TABLES

TABLE 1

COMPARISON OF IMPURITY LEVELS IN NUTRIENT SOURCES
(PPM by Weight)

Source	Li	Na	K	Al	Fe	Total
Natural	2.5	10.0	3.4	21.0	2.7	39.6
Cultured	1.3	8.3	0.5	6.0	0.5	16.6
Special	0.8	5.6	0.5	3.8	1.2	11.9
Converted	2.8	890	0.5	3.9	2.5	899.7

TABLE 2

TYPICAL IMPURITY LEVELS FOUND IN REAGENT GRADE MINERALIZERS
(PPM by Weight)

Mineralizer	K	Al	Fe	Total PPM
Na_2CO_3 (GC1)	0.7	0.5	0.5	1.7
NaOH (GC4)	1.6	0.5	0.5	2.6
NaOH (GC5)	0.7	0.5	0.5	1.7

TABLE 3

VARIATION OF ρ WITHIN A STONE AND BETWEEN STONES GROWN IN TOP AND BOTTOM TIERS IN A RUN

Position	ρ (cm^{-2})
Top Test #1	715
Top Test #2	610
Top Test #3	649
Top Test #4	723
Top Test #5	701
Top Test #6	867
Top Test #7	620
Top Test #8	565
Top Test #9	681
Bottom Test #1	704

$\bar{X}$ (Top Test) = $681 cm^{-2}$

S = $87 cm^{-2}$

TABLE 4

COMPARISON OF ETCH CHANNEL DENSITY AS A FUNCTION OF THE NUMBER OF 'AT' SAMPLES ETCHED

Number	4	8	15
Stone A	$270 \pm 76 cm^{-2}$	$280 \pm 24 cm^{-2}$	$281 \pm 39 cm^{-2}$
Stone B	$233 \pm 29 cm^{-2}$	$242 \pm 28 cm^{-2}$	$275 \pm 24 cm^{-2}$
Stone C	$165 \pm 59 cm^{-2}$	$153 \pm 9 cm^{-2}$	$129 \pm 10 cm^{-2}$

TABLE 5

STANDARDIZATION OF ETCHING TECHNIQUE

SOLUTION: 24.0 Molal NH_4HF_2

ETCH TIME: 2 Hours

ETCH TEMPERATURE: $75^{\circ}C \pm 5^{\circ}C$

SAMPLES PER LOAD: 4 to 8

SOLUTION VOLUME: 0.5 Liters

TABLE 6

COMPARISON OF GROWTH DATA FOR RUNS CONDUCTED IN CARBONATE MINERALIZER

Run #	$\bar{P}$ KPSI	$\bar{T}_c$ (°C)	$\overline{\Delta T}$ (°C)	$\bar{Z}$ (mm)	$\bar{Z}$ Range (mm)	$\bar{Z}$ Rate (mm/day)	Nutrient Type
CC1	8.7	340	5	39.5±0.6	2.4	0.54	Natural
CC8	8.8	341	4	41.0±1.6	7.9	0.49	Cultured
CC12	8.7	340	4	38.1±1.1	5.8	0.51	Cultured

TABLE 7

COMPARISON OF GROWTH DATA FOR RUNS CONDUCTED IN PRODUCTION VESSELS WITH HYDROXIDE MINERALIZER

Run #	$\bar{P}$ KPSI	$\bar{T}c$ (°C)	$\overline{\Delta T}$ (°C)	$\bar{Z}$ (mm)	$\bar{Z}$ Range (mm)	$\bar{Z}$ Rate (mm/day)	Nutrient Type
GC5	20.6	340	27	29.2±1.3	6.6	0.56	Cultured
GC6	22.5	342	19	42.6±0.8	5.6	0.78	Cultured
GC9	22.9	342	19	42.0±1.1	6.7	0.77	Cultured
GC11	21.1	342	19	42.1±1.0	6.2	0.79	Cultured
GC13	21.7	342	19	41.2±0.7	4.6	0.77	Cultured

TABLE 8

COMPARISON OF GROWTH DATA FOR RUNS CONDUCTED IN EXPERIMENTAL VESSEL WITH HYDROXIDE MINERALIZER

Run #	$\overline{P}$ KPSI	$\overline{Tc}$ (°C)	$\overline{\Delta T}$ (°C)	$\overline{Z}$ (mm)	$\overline{Z}$ Rate (mm/day)	Nutrient Type
GC2	24.0	348	25.4	31.2	.81	Cultured
GC4	23.2	347	20.2	35.3	.86	Cultured
GC7	23.8	347	18.8	31.6	.72	Converted
GC10	23.9	347	22.8	34.5	.85	Special

TABLE 9

COMPARISON OF CRITICAL DATA AMONG RUNS IN EXPERIMENTAL VESSEL

Run #	Seed Type	Seed Q ($x10^6$)	Seed ρ (cm^{-2})	Z Rate (mm/day)	Crystal Q ($x10^6$)	Crystal ρ (cm^{-2})	Nutrient Type
GC2	Regular	1.800	∿200	0.81	2.840	286	C
GC4	Swept	1.600	∿ 5	0.86	2.025	500	C
GC10	Chem. Pol.	2.342	∿100	0.85	2.342	231	S
GC7	+X	?	?	0.72	2.566	1652	G

TABLE 10

COMPARISON OF IMPURITY LEVELS IN CRYSTALS GROWN IN EXPERIMENTAL VESSEL RUNS

Run #	Nutrient Type	Li	Na	K	Al	Fe	Total PPM
		(PPM by weight)					
GC4	C	0.5	3.1	0.8	3.3	0.9	8.6
GC10	S	0.7	2.5	0.5	1.7	3.3	8.7
GC7	G	0.5	0.5	0.5	0.6	0.5	2.6

TABLE 11

COMPARISON OF RELATIVE DISTRIBUTION COEFFICIENTS
OF IMPURITIES IN EXPERIMENTAL AUTOCLAVE RUNS

Run #	k_{Li}	k_{Na}	k_{K}	k_{Al}	k_{Fe}
GC4	0.4	0.4	1.6	0.6	1.8
GC10	0.9	0.4	1.0	0.4	2.8
GC7	0.2	0.0	1.0	0.2	0.2

TABLE 12

COMPARISON OF CRITICAL DATA AMONG CRYSTALS GROWN IN CC5

Seed Type	Seed Q ($\times 10^6$)	Seed ρ (cm^{-2})	Seed Etch	Ftch Time	Crystal Q ($\times 10^6$)	Crystal ρ (cm^{-2})
Swept	2.2	<5	ABF	5	2.3	346
Reg.	2.3	400	ABF	5	2.2	258
Reg.	2.4	231	ABF	60	2.1	349
Reg.	2.3	400	HF	5	2.2	335

TABLE 13

COMPARISON OF GROWTH RATE, $\overline{Q}$ AND $\overline{\rho}$ AS A FUNCTION OF SEED PREPARATION CONDITIONS EMPLOYED IN GC6

Etching Conditions	$\overline{Z}$ Rate (mm/day)	$\overline{Q}$ ($\times 10^6$)	$\overline{\rho}$ (cm^{-2})
7.0m ABF - 5 min.	0.822	1.952	159
48% HF - 5 min.	0.787	1.938	225
48% HF + 40% AF - 5 min.	0.794	1.846	256
$\overline{X}$	0.801	1.912	213
S	0.018	0.071	75
7.0m ABF - 10 min.	0.789	1.982	145
48% HF - 10 min.	0.798	1.990	179
48% HF + 40% AF - 10 min.	0.795	1.925	254
$\overline{X}$	0.794	1.967	193
S	0.131	0.156	61

TABLE 14

COMPARISON OF GROWTH RATE, $\bar{Q}$ AND $\bar{\rho}$

AS A FUNCTION OF ETCHANT IN CC6

Parameter/Etchant	ABF	HF	HFAF
$\bar{Z}$ Rate (mm/day)	0.805	0.792	0.795
S	0.021	0.008	0.016
$\bar{Q}$ ($\times 10^6$)	1.967	1.967	1.885
S	0.147	0.041	0.150
$\bar{\rho}$ (cm^{-2})	152	202	255
S	21	70	69

TABLE 15

COMPARISON OF GROWTH RATE, $\overline{Q}$ AND $\overline{\rho}$ AS A FUNCTION OF SEED PREPARATION CONDITIONS IN GC9 AND GC11

Etching Conditions	$\overline{Z}$ Rate (mm/day)	$\overline{Q}$ ($\times 10^6$)	$\overline{\rho}$ (cm^{-2})	Run No.
7.0 molal ABF - 5 min.	0.770	2.09	139	GC9
7.0 molal ABF - 15 min.	0.761	2.23	270	
7.0 molal ABF - 30 min.	0.766	2.09	542	
$\overline{X}$	0.766	2.14	317	
S	0.005	0.08	206	
7.0 molal ABF - 15 min.	0.782	1.761	220	GC11
AF + HF - Chem. Polish.	0.787	1.84[a]	304	

TABLE 16

COMPARISON OF GROWTH RATE, $\overline{Q}$ AND $\overline{\rho}$ AS A FUNCTION OF SEED CONDITION

Seed Condition	$\overline{Z}$ Rate (mm/day)	$\overline{Q}$ ($x10^6$)	$\overline{\rho}$ (cm^{-2})
No Strain - Pure Z	0.802	1.997	152
Strain - Pure Z	0.851	1.490	352
Strain - Z Seed Cut From +X	0.721	2.566	1652

TABLE 17

COMPARISON OF IMPURITY LEVELS IN AS-GROWN CRYSTALS WITH RESPECT TO CRITICAL PARAMETERS IN CC6

Seed Prep.	Crystal Q ($x10^6$)	Crystal ρ (cm^{-2})	Li	Na	K	Al	Fe	Total
			(PPM by weight)					
ABF - 5'	1.908	135	0.8	1.7	0.5	3.3	0.5	6.8
HF + AF - 5'	1.908	322	0.6	1.1	0.5	2.1	1.1	5.4

TABLE 18

COMPARISON OF CRITICAL DATA AMONG CRYSTALS GROWN IN GC1

Seed Prep.	Seed Q ($x10^6$)	Seed ρ (cm^{-2})	Crystal Q ($x10^6$)	Crystal ρ (cm^{-2})
ABF - 5'	1.80	169	1.50	158
HF - 5'	1.80	169	1.54	221
ABF - 5'	1.30	500	1.41	208
ABF - 5'	1.30	500	1.44	278

TABLE 19

COMPARISON OF GROWTH RATE, $\bar{Q}$ AND $\bar{\rho}$ AS A FUNCTION OF SEED PREPARATION CONDITIONS EMPLOYED IN GC8

Etching Conditions	Seed Cond.	$\bar{Z}$ Rate (mm/day)	$\bar{Q}$ ($\times 10^6$)	$\bar{\rho}$ (cm^{-2})
HF + AF - 5 min.	Strained	0.499	1.700	372
ABF - 5 min.	Strained	0.489	1.500	352
HF + AF - 10 min.	Clear	0.459	2.000	155
HF - 10 min.	Clear	0.459	1.830	332
$\bar{X}$	———	0.477	1.760	303
S	———	0.021	0.211	100

TABLE 20

COMPARISON OF IMPURITY LEVELS IN CRYSTALS
GROWN FROM SEEDS OF DIFFERENT QUALITY

Seed Cond.	Crystal Q ($\times 10^6$)	Crystal ρ (cm^{-2})	Li	Na	K	Al	Fe	Total
			(PPM by weight)					
Strained	1.700	372	6.9	11.0	0.5	23.0	9.0	50.4
Clear	1.810	185	1.4	7.1	0.5	4.2	0.6	13.8

TABLE 21

TYPES OF BLANKS TO BE FABRICATED ON A RUN BASIS

Run Nos.	ϕ	θ	Dia. (mm)	Thickness (mm)
GC1	$21^{\circ}56'$	$34^{\circ}01'$	15	1.65
GC1	$21^{\circ}56'$	$34^{\circ}01'$	14	1.22
GC1	$21^{\circ}56'$	$34^{\circ}01'$	15	1.22
GC1	0	$35^{\circ}34'$	15	1.65
GC1	0	$35^{\circ}34'$	15	1.14
GC2	0	$35^{\circ}34'$	15	1.65
GC2	0	$35^{\circ}34'$	15	1.14
GC4	0	$35^{\circ}34'$	15	1.65
GC6,	0	$35^{\circ}34'$	15	1.65
GC9, &	0	$35^{\circ}34'$	15	1.14
GC11	0	$35^{\circ}34'$	14	1.14
GC6,	$21^{\circ}56'$	$34^{\circ}01'$	15	1.65
GC8, &	$21^{\circ}56'$	$34^{\circ}01'$	15	1.22
GC9	$21^{\circ}56'$	$33^{\circ}57'$	15	1.93
	$21^{\circ}56'$	$34^{\circ}01'$	14	1.22
GC7 & GC10	$21^{\circ}56'$	$33^{\circ}50'$	6.35	0.22

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